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PATENT SPECIFICATION

NO DRAWINGS

1,111,708

1,111,708



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No. 34225/66.

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Int. Cl.: —C 11 d 5/00

COMPLETE SPECIFICATION

Antimicrobial Detergent Compositions

We, THE PROCTER & GAMBLE COMPANY, a corporation organised under the laws of the State of Ohio, United States of America, of 301 East Sixth Street, Cincinnati, Ohio,

5 United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

10 This invention relates to detergent compositions having antimicrobial properties. More particularly it relates to detergent compositions containing a heavy metal salt of 2-pyridinethiol-1-oxide as an antimicrobial agent, said compositions having improved activity by virtue of the presence of certain polyethylenimine or alkoxylated polyethylenimine polymers.

15 It is known that certain salts of 2-pyridinethiol-1-oxide (hereinafter referred to as "pyridinethione") have outstanding antimicrobial and antidandruff properties when incorporated in detergent compositions. See,

20 for example British patent specification No. 957,458. The unique sustained antimicrobial activity of these compounds in detergent compositions appears to be due in part to the fact that particles of these pyridinethione salts are deposited on surfaces of materials washed in said compositions and are retained thereon through the rinsing step. It has been found that only a relatively small proportion of the pyridinethione salt present in a detergent composition actually deposits on the washed surface and survives the rinsing operation.

25 Since sustained antimicrobial or antidandruff activity of pyridinethione salts is in part a function of the quantity of the particles deposited and retained on surfaces to which

they are applied, measures which enhance deposition or promote retention will permit either reduction of the quantity of the pyridinethione salt required to attain a given level of antimicrobial or antidandruff activity or will increase the activity attainable using a given concentration of such salt.

30 It is an object of this invention to provide detergent compositions capable of imparting sustained antimicrobial properties to surfaces washed therewith.

35 It is a further object of this invention to provide shampoo compositions which have high levels of antidandruff activity relative to the concentrations of particulate antimicrobial agents contained therein.

40 It is a still further object of this invention to provide a method for enhancing the deposition of particulate substances from detergent compositions and retention of said substances and washed surfaces.

45 These and other objects will become apparent from the following description.

50 It has now been found that the deposition and retention of particulate matter from detergent compositions is markedly enhanced by the presence of certain cationic polymers. More particularly, water-soluble polymers of ethylenimine or "alkoxylated" polyethylenimines (i.e. polyethylenimine reacted with ethylene oxide or propylene oxide) when mixed with particulate heavy metal salts of 2-pyridine-thio-1-oxide prior to incorporating these materials in detergent compositions, have the effect of enhancing deposition and retention of said salts on surfaces which are washed therewith.

55 A variety of cationic polymers have been suggested for use in shampoo compositions to improve hair manageability. For example, polyethylenimine resins are described as suit-

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able for this purpose in British patent specification No. 1,078,075. However, this application does not suggest the inclusion of particulate antidandruff agents.

5 According to the present invention, a detergent composition comprises an organic surfactant, a water-soluble cationic polymer selected from the group consisting of polyethylenimines and alkoxyLATED polyethylenimines having molecular weight greater than 100, and a particulate heavy metal salt of 2-pyridinethiol-1-oxide.

10 Organic surfactants which can be used in the compositions of this invention are anionic, amphoteric, polar nonionic, zwitterionic or cationic or mixtures thereof. This component can suitably comprise from 2% to 95% by weight of the total composition. Operable anionic organic surfactants are, for example, the water-soluble salts of sulphated or sulphonated organic reaction products having in their molecular structure an alkyl group containing from 8 to 20 carbon atoms and a sulphuric acid ester or 15 sulphonic acid radical. Such surfactants include the sodium or potassium alkyl sulphates, especially those derived by sulphation of higher alcohols produced by reduction of tallow or coconut oil glycerides; sodium or 20 potassium alkyl benzene sulphonates, especially those of the types described in British patent specification No. 645,129, in which the alkyl group contains from 9 to 15 carbon atoms; sodium alkyl glycetyl ether sulphonates, especially those ethers of higher alcohols obtained from tallow and/or coconut oil; 25 sodium coconut oil fatty acid monoglyceride sulphates and sulphonates; sodium salts of sulphuric acid esters of the reaction product of one mole of a higher alcohol (i.e. tallow or coconut oil alcohols) and about 3 moles of ethylene oxide; and salts of condensation products of fatty acids with sarcosine, e.g., triethanolamine N-acyl sarcosinate, the acyl 30 radicals being derived from coconut oil fatty acids.

40 Preferably, anionic organic surfactants of the high sudsing type are used for the shampoo embodiments of this invention. Thus, alkyl glycetyl ether sulphonates, N-acyl sarcosinates, and alkyl ether ethylene oxide sulphates as described above are used to 45 special advantage. These and the foregoing surfactants can be used in the form of their sodium, potassium or lower alkanolamine (i.e. containing one or more alkanol radicals each having from 1 to 3 carbon atoms, e.g. triethanolamine) salts.

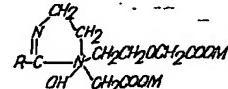
50 Conventional soaps are also operable anionic surfactants for the purposes of this invention. Suitable soaps include the sodium, potassium, and lower alkanolamine salts of fatty acids occurring in coconut oil, soybean oil, castor oil or tallow, or synthetically produced fatty acids may be used.

55 Polar nonionic surfactants can be used, either alone or in admixture with anionic and/or amphoteric surfactants. Surfactants of this class can serve to enhance lathering and cleaning properties of anionic detergents. By "polar nonionic surfactant" is meant a surfactant in which the hydrophilic group contains a semi-polar bond directly between two atoms, e.g. $N \rightarrow O$, $P \rightarrow O$, $As \rightarrow O$, and $S \rightarrow O$. (The arrow is the conventional representation of a semi-polar bond.) There is charge separation between the two directly bonded atoms, but the surfactant molecule bears no net charge and does not dissociate into ions.

60 Preferred polar nonionic surfactants for use in the present compositions are amine oxides of the general formula $R_1R_2R_3N \rightarrow O$, wherein R_1 is an alkyl, alkenyl, or mono-hydroxy-alkyl radical having from 10 to 16 carbon atoms, and R_2 and R_3 are each methyl, ethyl, propyl, ethanol or propanol radicals. An especially preferred amine oxide is dodecyl dimethyl amine oxide.

65 Other operable polar nonionic surfactants are the phosphine oxides having the general formula $R_1R_2R_3P \rightarrow O$, wherein R is an alkyl, alkenyl or monohydroxyalkyl radical ranging in chain length from 10 to 18 carbon atoms, and R_2 and R_3 are each alkyl or mono-hydroxyalkyl radicals containing from 1 to 3 carbon atoms. A preferred phosphine oxide is dodecyl dimethyl phosphine oxide.

70 Suitable amphoteric surfactants include the alkyl beta-iminodipropionates, $RN(C_2H_4COOM)_2$, alkyl beta-amino propionates, $RN(H)C_2H_4COOM$, and long chain imidazole derivatives having the general formula:



75 In each of the above formulae R is an acyclic hydrophobic group containing from 8 to 18 carbon atoms and M is a cation to neutralize the charge of the anion, e.g. an alkali metal such as sodium or potassium, ammonium or substituted ammonium cations. Specific operable amphoteric surfactants include the disodium salt of lauroyl-cycloimidinium-1-ethoxyethionic acid-2-ethionic acid, dodecyl beta-alanine, and the inner salt of 2-trimethylamino lauric acid. As zwitterionics, the substituted betaines such as alkyl dimethyl ammonio acetates wherein the alkyl radical contains from 12 to 18 carbon atoms can also be used. Several examples of this class of zwitterionic surfactants are set forth in Canadian patent specification No. 696,355.

80 Especially preferred shampoo compositions in accordance with this invention contain non-soap anionic and amphoteric, zwitterionic or polar nonionic surfactants, and mixtures

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thereof. For example, excellent results are obtained with shampoo compositions containing as the detergent component (1) from 4% to 20% by weight of the total composition of a non-soap organic anionic surfactant and (2) from 4% to 20% by weight of the total composition of a polar anionic, zwitterionic or amphoteric surfactant.

Although nonionic and cationic surfactants are not preferred for the purposes of this invention they can nevertheless be used without substantial loss of the advantageous effects of the cationic polymers on deposition and retention of particulate matter on washed surfaces. Nonionic surfactants may be described as compounds produced by the condensation of alkylene oxide groups (hydrophilic in nature) with an organic hydrophobic compound, which may be aliphatic or alkyl aromatic in nature. As those skilled in the art are well aware, the length of the hydrophilic or polyoxyalkylene radical required for condensation with any particular hydrophobic group can be readily adjusted to yield a water-soluble compound having the desired degree of balance between hydrophilic and hydrophobic elements.

For example, a well-known class of nonionics is made available on the market under the Trade Mark "Pluronic". These compounds are formed by condensing ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol. The hydrophobic portion of the molecule, of course, exhibits water insolubility. Its molecular weight is of the order of 1500 to 1800. The addition of polyoxyethylene radicals to this hydrophobic portion tends to increase the water solubility of the molecule as a whole. Liquid products are obtained up to the point where polyoxyethylene content is about 50% of the total weight of the condensation product.

Suitable nonionics also include the polyethylene oxide condensates of alkyl phenols, e.g. the condensation products of alkyl phenols having 6 to 12 carbon atoms, either straight chain or branch chain, in the alkyl group with ethylene oxide in amounts equal to 10 to 25 moles of ethylene oxide per mole of alkyl phenol. The alkyl substituent in such compounds may be derived from polymerized propylene, diisobutylene, octane, or nonane, for example.

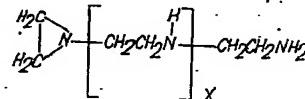
Other suitable nonionics may be derived by the condensation of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylene diamine. Here again, a series of compounds may be produced, depending on the desired balance between hydrophobic and hydrophilic elements. For example, compounds (molecular weight from about 5,000 to about 11,000) of about 40% to 80% by weight of polyoxyethylene content and resulting from the reaction of

ethylene oxide groups with a hydrophobic base constituted of the reaction product of ethylene diamine and excess propylene oxide, said base having a molecular weight of the order of 2500 to 3000, are satisfactory.

Further satisfactory nonionics include the condensation product of aliphatic alcohols having from 8 to 18 carbon atoms, either straight chain or branched chain, with ethylene oxide, an example being a coconut alcohol/ethylene oxide condensate having from 10 to 30 moles of ethylene oxide per mole of coconut alcohol, the coconut alcohol fraction having from 10 to 14 carbon atoms.

Cationic surfactants which can be used in the compositions of this invention include distearyl dimethyl ammonium chloride, stearyl dimethyl benzyl ammonium chloride, coconut alkyl dimethyl benzyl ammonium chloride, cocoonut alkyl dimethyl ammonium chloride, cetyl pyridinium chloride, and cetyl trimethyl ammonium bromide.

The compositions of this invention should usually contain from 0.1% to 4.0% by weight of polyethylenimine or alkoxylated polyethylenimine cationic polymers. It is believed that the structural formula of the backbone of polyethylenimine is:



wherein x represents a whole number of sufficient magnitude to yield a polymer of molecular weight greater than 100. Branched chains occur along the polymeric backbone and the relative proportions of primary, secondary and tertiary amino groups present in the polymer will vary, depending on the manner of preparation. The distribution of amino groups in a typical polyethylenimine is approximately as follows:

$-\text{CH}_2\text{CH}_2\text{--NH}_2$	30%	105
$-\text{CH}_2\text{--CH}_2\text{--NH--}$	40%	
$-\text{CH}_2\text{--CH}_2\text{--N--}$	30%	

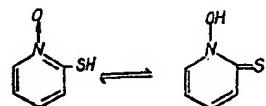
The polyethylenimine is characterized herein in terms of molecular weight. Such polymers can be prepared, for example, by polymerizing ethylenimine in the presence of a catalyst such as carbon dioxide, sodium bisulphite, sulphuric acid, hydrogen peroxide, hydrochloric acid or acetic acid. Specific methods are described in U.S. patent specifications Nos. 2,182,306, 3,033,746, 2,208,095, 2,806,839 and 2,553,696.

Similarly, alkoxylated polyethylenimine can be prepared, for example, by reacting one part by weight ethylene oxide or propylene oxide with one part by weight of polyethylen-

imine prepared as described above and having a molecular weight greater than 100. Preferably, the weight ratio of polyethylenimine to alkylene oxide is at least 1:1.

- 5 The polymers suitable for use in this invention must have an average molecular weight greater than 100. Preferably it is less than about 500,000. If the molecular weight of the polymer is less than about 100, no substantial enhancement of deposition occurs. Best results are obtained with polymers having a molecular weight of from 3,000 to 100,000, and the polymers are most preferably employed in the detergent composition at a concentration within the range from 0.25% to 2.00% by weight.

10 The antibacterial agents employed herein are salts of 2-pyridinethiol-1-oxide which has the following structural formula in tautomeric form, the sulphur atom being attached to the number 2 position of the pyridine ring:



2-pyridinethiol-1-oxide 1-hydroxy-2-pyridinethione

15 Heavy metal salts of the above compounds are sparingly soluble and have a high degree of antibacterial activity. Preferred salts include zinc, cadmium, tin and zirconium 2-pyridinethiol-1-oxides.

20 These salts are used in particulate form, with average particle sizes ranging from 0.5 to 30 microns. The quantity of pyridinethione salt employed can suitably range from 0.1% to 10% and preferably is from 0.5% to 2.0% by weight. It is preferred that the weight ratio of pyridinethione salt to the cationic polymer in the detergent compositions of this invention be from 1:40 to 100:1, preferably from 1:4 to 8:1.

25 Very suitable detergent compositions of this invention comprise:

(1) an organic surfactant, (2) a particulate pyridinethione salt selected from zinc, cadmium, zirconium and tin 2-pyridinethiol-1-oxide and (3) a cationic polymer selected from polyethylenimine and a reaction product of a polyethylenimine having a molecular weight greater than 100 and ethylene oxide or propylene oxide, the weight ratio of polyethylenimine to ethylene oxide or propylene oxide in said reaction product being at least 1:1, the average molecular weight of said cationic polymer being from 3,000 to 100,000, the weight ratio of pyridinethione salt to polymer being within the range from 1:4 to 8:1.

30 Preferred detergent compositions in accordance with this invention are especially adapted

to washing hair and scalp and comprise water and from 10% to 35% by weight of at least one organic surfactant, which may for example be a non-soap anionic, polar non-

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ionic, amphoteric or zwitterionic surfactant; from 0.25% to 2.0% by weight of a polyethylenimine or alkoxyated polyethylenimine polymer, for example, one having an average molecular weight within the range from 3,000 to 100,000; from 0.5% to 2.0% by weight of the heavy metal, e.g. zinc, cadmium, tin, or zirconium, salt of 2-pyridinethiol-1-oxide.

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10 Detergent compositions in accordance with this invention can be prepared by methods well known in the art; however, it has been found that especially good results are obtained when the polyethylenimine or alkoxy-

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EXAMPLE I
A shampoo composition was prepared having the following formulation:

% by Weight
Sodium coconut alkyl glyceryl ether sulphonate (about 23% diglyceryl and the balance substantially monoglyceryl)
25.0
Sodium tallow alkyl glyceryl ether sulphonate (about 23% diglyceryl and the balance substantially monoglyceryl; the tallow alkyls
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	correspond to those of substantially saturated tallow alcohols and contain approx. 2% C ₁₄ , 32% C ₁₆ and 66% C ₁₈)	Polyethylenimine*	0.75
5	Sodium chloride	Cadmium 2-pyridinethiol-1-oxide (Average particle size 3.0 microns)	0.25
	Sodium sulphate	Water, NaOH to adjust to pH 8.5	Balance
	Sodium N-lauroyl sarcosinate	* A water-soluble polymer having a molecular weight of 50,000 to 100,000 and viscosity of 2.5 centipoises (absolute viscosity) in a 1% by weight aqueous solution measured with an Ostwald Viscometer at 100°F	55
10	N-coconut acyl sarcosine		
	Diethanolamide of coconut fatty acids		
	Acetylated lanolin		
	Perfume		
	Colour		
15	Zinc 2-pyridinethiol-1-oxide*	This composition has excellent antimicrobial properties and in usage imparts sustained antimicrobial activity to surfaces washed therewith. The amine oxide can be replaced, in whole or in part, with disodium coconut beta-iminodipropionate, the disodium salt of lauroylcycloimidinium-1-ethoxy-ethionic acid-2-ethionic acid, or dodecyl ammonio acetate, with substantially equivalent results.	60
	Polyethylenimine** / ethylene oxide reaction product (weight ratio 1:1, molecular weight 80,000—120,000)		65
20	Water		
	* Average particle size 2 microns		
	** (Molecular weight 40,000—60,000)		

25 The zinc pyridinethione and ethoxylated polyethylenimine were uniformly admixed and added to and uniformly mixed with the balance of the components. The resulting product was a stable cream having excellent cosmetic and antidandruff properties. The degree of deposition of zinc pyridinethione from this composition was much greater than the degree of deposition attained with a similarly formulated product which contained no cationic polymer. Residual antimicrobial activity of surfaces washed with this composition is markedly greater as compared to surfaces washed with a control product without the polyethylenimine-based polymer.

EXAMPLE II
Another shampoo formulation in accordance with this invention is formulated as follows:

	% by Weight	% by Weight	
		Triethanolamine coconut alkyl sulphate	75
45	10.0	Monoethanol amide of coconut fatty acid	20.0
	10.0	Magnesium aluminium silicate	4.5
	5.0	Methylcellulose	0.9
	10.0	Dye	0.23
		Perfume	0.008
		Zinc 2-pyridinethiol-1-oxide*	0.8
		Polyethylenimine** / ethylene oxide reaction product (weight ratio 4:1, molecular weight 50,000)	1.0
		* Average particle size 1.5 microns	0.5
		** Molecular weight 10,000	85

This composition provides a substantial degree of antidandruff effect when used in the customary fashion. The degree of deposition and retention of particulate zinc pyridinethione on the hair and scalp after shampooing with this product is substantially greater than is attained with a similar composition without the polyethylenimine/ethylene oxide reaction product.

		IV	V	VI	VII	Examples % by weight	VIII	IX	X	XI
5	Sodium coconut alkyl (ethoxy), sulphate	20		5	10	7.5				
	Sodium lauroyl sarcosinate		25		10					
	Sodium dodecyl Benzene sulphonate			5	5		25			
	2-trimethylamine lauric acid inner salt									
	Triethanolamine coconut alkyl mono-glyceride sulphonate					7.5				
10	Potassium coconut soap				5			20		
	Ethanol		2.0		2.5		0.5		1.0	
	Polyethylenimine*									
	Polyethylenimine*/propylene oxide reaction product**			1.5	2.5	0.5		2.0		
15	Tin 2-pyridinethiol-1-oxide (average particle size 7 microns)	1.0		0.5		2.0		0.1		
	Zirconium 2 - pyridinethiol - 1 - oxide (average particle size 4 microns)		1.0		0.5		2.5		1.5	
	Water				Balance					
20	* (Molecular weight 10,000)									
	** (Weight ratio 2:1, molecular weight 30,000)									

Each of the above compositions imparts a residual antimicrobial activity to surfaces washed therein which is substantially greater than is attainable with similar compositions without the polymeric component.

In Example XI, distearyl dimethyl ammonium chloride, stearyl dimethyl benzyl ammonium chloride, or dicoconut alkyl dimethyl ammonium chloride can be used in place of sodium dodecyl benzene sulphonate without loss of the improved deposition and retention of zirconium 2-pyridinethiol-1-oxide particles effected by the polyethylenimine.

In Example IV, sodium coconut alkyl (ethoxy), sulphate can be replaced with the condensation product of ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol and having a molecular weight of 1600 or the condensation product of octyl phenol and ethylene oxide using a mole ratio of 1:15, with substantially equivalent results.

The enhanced deposition and retention of pyridinethione salts was demonstrated as follows: A control composition was formulated as in Example I, but omitting the polyethylenimine/ethylene oxide reaction product.

A composition similar in formation but containing 0.5% of polyethylenimine having a molecular weight of 50,000 was prepared and designated test composition "A". A test composition designated "B" which differed from the control composition in containing 0.5% of the polyethylenimine of composition A and 1.0% of zinc 2-pyridinethiol-1-oxide having an average particle size of 2 microns, rather than 2.0% of this latter component as in the control composition, was also prepared.

The hair of 16 female subjects was shampooed by experienced beauty shop operators who washed half of the hair and scalp of

each subject with the control composition. The other half of the subject's hair and scalp was washed in the assigned test composition. The test and control composition were used *ad libitum*, in quantities sufficient to provide a good lather. After lathering for 45 seconds, the hair was rinsed and the compositions were reapplied, lathered for 45 seconds and rinsed again. The hair was then dried. A sample of cornified epithelium from both the control and test halves of each subject's scalp was obtained by applying cellulose adhesive tape against the scalp. The tape was then placed on a glass slide with the adhesive in contact with the glass. The slide was examined with a polarizing microscope at approximately 400 diameters with polaroids crossed. While the cornified epithelium exhibited some degree of birefringence, the highly anisotropic properties of the particular zinc 2-pyridinethiol-1-oxide made it readily visible under such viewing conditions. The relative quantity of particulate zinc 2-pyridinethiol-1-oxide was then graded on a 0 to 4 scale, with a grade of "4" indicating heavy deposition, and "0" indicating substantially no deposition.

The following results were obtained:

Composition	Average Degree of Deposition
Control	2.3
A	3.4
B	2.6

It can be seen from the above results that deposition and retention of zinc 2-pyridinethiol-1-oxide was substantially greater from a detergent composition which contained 0.5% of polyethylenimine as compared to the control composition which contained the same amount of zinc 2-pyridinethiol-1-oxide with-

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out polymer. Similarly, composition B which contained only 1.0% of zinc 2-pyridinethiol-1-oxide yielded a somewhat higher degree of deposition and retention than the control composition which contained twice as much of this salt, but no polymer.

In like manner the relative deposition of zinc 2-pyridinethiol-1-oxide from a detergent composition containing various concentrations of ethoxylated polyethylenimine was demonstrated as follows: The following compositions were prepared. 10

		% By Weight Composition				
		Control	C	D	E	F
15	Sodium coconut alkyl glyceryl ether sulphonate*	25.0	25.0	25.0	25.0	25.0
20	Sodium tallow alkyl glyceryl ether sulphonate	3.0	3.0	3.0	3.0	3.0
	Sodium chloride	6.5	6.5	6.5	6.5	6.5
	Sodium sulphate	3.1	3.1	3.1	3.1	3.1
25	Sodium N-lauroyl sarcosinate	3.8	3.8	3.8	3.8	3.8
	N-coconut acyl sarcosinate	1.2	1.2	1.2	1.2	1.2
	Coconut acyl diethanolamide	2.0	2.0	2.0	2.0	2.0
	Acetylated lanolin	1.0	1.0	1.0	1.0	1.0
	Perfume	0.4	0.4	0.4	0.4	0.4
	Colour	0.04	0.04	0.04	0.04	0.04
30	Zinc 2-pyridinethiol-1-oxide (average particle size 2 microns)	2.0	1.0	0.5	1.0	0.5
	Polyethylenimine/ethylene oxide reaction product*	0	1.0	1.0	2.0	2.0
	Water				Balance	

* Same as Example I

35 Each of the compositions was tested in the manner described supra, using a test composition and control composition on each of the test subjects. The results attained were as follows:—

	Average Degree of Deposition
Composition C (8 subjects)	3.3
Control (same 8 subjects)	3.0
Composition D (8 subjects)	1.0
Control (same 8 subjects)	2.4
Composition E (4 subjects)	4.0
Control (same 4 subjects)	3.3
Composition F (8 subjects)	3.4
Control (same 8 subjects)	3.3

50 It can be seen that the degree of deposition attained with composition C containing only half as much zinc 2-pyridinethiol-1-oxide as the control was nevertheless greater than the control. Composition D, which contains 1.0% polymer and only 1/4 as much zinc 2-pyridinethiol-1-oxide as the control, displayed only moderately less deposition than the control. Composition E, which contains 2% polymer and only half as much zinc 2-pyridinethiol-1-oxide as the control, provides somewhat greater deposition than the control. Composition F, containing 2.0% polymer and only 1/4 as much zinc 2-pyridinethiol-1-oxide as the control, provides a degree of deposition approximately equal to the control.

WHAT WE CLAIM IS:—

1. A detergent composition comprising an organic surfactant, a water-soluble cationic polymer selected from the group consisting of polyethylenimines and alkoxylated polyethylenimines having molecular weight greater than 100, and a particulate heavy metal salt of 2-pyridinethiol-1-oxide. 70

2. A detergent composition according to claim 1 in which the cationic polymer has an average molecular weight of from 3,000 to 100,000. 75

3. A detergent composition according to claim 1 or 2 in which the cationic polymer is polyethylenimine. 80

4. A detergent composition according to claim 1 or 2 in which the cationic polymer is a reaction product of polyethylenimine and ethylene oxide, the weight ratio of polyethylenimine to ethylene oxide being at least 1:1. 85

5. A detergent composition according to claim 1 or 2 in which the cationic polymer is a reaction product of polyethylenimine and propylene oxide, in the weight ratio of polyethylenimine to propylene oxide being at least 1:1. 90

6. A detergent composition according to any of the preceding claims in which the particulate heavy metal salt of 2-pyridinethiol-1-oxide is a zinc, cadmium, zirconium or tin salt. 95

7. A detergent composition according to any of the preceding claims in which the particulate heavy metal salt of 2-pyridinethiol-1-oxide has a mean particle size of from 0.5 to 30 microns.
8. A detergent composition according to any of the preceding claims in which the organic surfactant is a non-soap anionic, polar nonionic zwitterionic or amphoteric detergent, or a mixture thereof.
9. A detergent composition according to claim 8 in which the organic surfactant is a sodium alkyl glyceryl ether sulphonate in which the alkyl group is derived from tallow and/or coconut oil.
10. A detergent composition according to any one of the preceding claims which comprises from 2 to 95% by weight of the organic surfactant.
11. A detergent composition according to claim 10 which comprises from 10 to 35% by weight of the composition of organic surfactant.
12. A detergent composition according to any one of claims 1 to 9 which comprises from 4% to 20% by weight of the total composition of non-soap organic anionic surfactant and from 4% to 20% by weight of the total composition of a polar nonionic, zwitterionic or amphoteric surfactant.
13. A detergent composition according to any one of the preceding claims which comprises from 0.1% to 4% by weight of the composition of the cationic polymer.
14. A detergent composition according to claim 13 which comprises from 0.25% to 2%
- by weight of the composition of the cationic polymer.
15. A detergent composition according to any one of the preceding claims which comprises from 0.1% to 10% by weight of the composition of the heavy metal salt of 2-pyridinethiol-1-oxide.
16. A detergent composition according to claim 15 which comprises from 0.5% to 2% by weight of the composition of the heavy metal salt of 2-pyridinethiol-1-oxide.
17. A detergent composition according to any one of the preceding claims in which the weight ratio of the heavy metal salt to cationic polymer is from 1:40 to 100:1.
18. A detergent composition according to claim 17 in which the weight ratio of the heavy metal salt to the cationic polymer is from 1:4 to 8:1.
19. An aqueous detergent composition according to any one of claims 1 to 9, 17 or 18 which comprises water and from 10% to 35% by weight of organic surfactant, from 0.25% to 2% by weight of the cationic polymer, and from 0.5% to 2% by weight of the heavy metal salt of 2-pyridinethiol-1-oxide.
20. A detergent composition according to claim 1 and substantially as described in any one of the Examples.

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